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The Effect of Humic Acid and Silicic Acid on P Adsorption by Amorphous Minerals

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Abstract

Andisol is a soil with high P adsorption, this is due to high content in reactive amorphous materials. The present study was conducted to compare humic acid and silicate acid in blocking the P adsorption on amorphous minerals. The results indicated that the old and young formation of parent materials were not different in reactivity of the amorphous minerals and able to adsorb P > 98 % and fit with the Freundlich equation. Application of humic acid and silicate acid with rate of 100 mg/l, respectively, was not effective in decreasing P adsorption. However, silicate acid was a little bit better than humic acid in decreasing P adsorption, in case of pH 4 either pH 6. Infrared spectral characteristics of the amorphous material indicated that the absorption bands of the first region appeared at a range of 3440-3510 cm^{-1}, the band due to stretching vibration of hydroxyl (OH) groups either as structural OH or as adsorbed water. The absorption bands of HOH from adsorbed water appeared ranging from 1639-1655 cm^{-1}. The maximum adsorption bands were observed appeared ranging from 910-972 cm^{-1}, the bands are due stretching vibration of Si-O-Al for allophane with low Si/Al ratio, whereas allophane with high Si/Al ratio appeared at 1033 - 1030 cm^{-1}. In general, the addition of humic acid and silicate acid caused the peak OH, Si-O-Al and Si-O adsorption move to the right and increase the adsorption intensity.

Keywords: Humic Acid; Silicic Acid; P adsorption; Amorphous minerals; infrared spectral

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1. Introduction

In general, Andisols are predominated by amorphous materials such as Al-oxides, Fe-oxides, allophane, and imogolite [1-3]. The variable charge mineral constituents (≡Al-OH and ≡Fe-OH) has an important role in adsorbing some oxyanions. Due to their high surface area and reactivity, they strongly retain anions such as phosphate [4], borate [5], carboxylate acids (acetate, oxalate, citrate) [6], molibdate [7], silicate [8], sulphate [9], and organic matter [10] and either as adsorbed species or as a reaction products. The principal sorption mechanism is ligand exchange involving the formation of inner-sphere surface complexes [11]. Humic acid as a product of soil organic matter decomposition has been known contributing in blocking a sesquioxide active adsorption site to reduce P sorption [12]. Silikat (SiO_4^{4-}) as an anion with high afinity may capability into replace other anions such as: phosphate, sulfate and halide on adsorption complexes [13]. The study was conducted to find out the effect of Humic and Silisic acids application on P adsorption by amorphous material and its change in chemical and infrared spectral characteristics.

2. Materials and Methods

Soil samples were taken out from B/C Horizon from Mt.Slamet (YS and OS as represent of Young Slamet and Old Slamet formation, respectively), Mt.Dieng (YD and OD as represent of Young Dieng and Old Dieng formation, respectively), Mt.Merbabu (YM and OM as represent of Young Merbabu and Old Merbabu formation, respectively) and Mt.Lawu (YL and OL as represent of Young Lawu and Old Lawu formation, respectively), Central Java, Indonesia. Soil sampling considered a representation of the age of the parent materials (old and young formation). Characterization of the amorphous minerals was conducted for clay fraction by applying the pipette method (Stock's Principle). The study of P adsorption was carried out of the series of $Na(H_2PO_4)$ with 0, 10, 20, 30, 40, and 50 mM. The system of the solution was adjusted to pH 4 and pH 6 and as a background solution 10 mM NaCl. Before application of $Na(H_2PO_4)$ solution, the amount of 0,6 gr l^{-1} allophane has been treated with each of 100 mg L^{-1} humic acid (HA) and silicic acid (SA). The amount of P adsorption was calculated by subtracting the amount of P addition with P concentration remained in the equilibrium condition. The blue complexation method (NH_4-molibdate) was applied for measuring P concentration in the solution. The Freundlich equation ($x/m = k\ C^{1/n}$) was applied for describing the P adsorption pattern. x/m = the amount of adsorbed P (μg g^{-1}), C = P concentration in equilibrium condition (μg ml^{-1}), n = energy bonding (afinity), k = sorption capacity. Infrared spectral characteristics were run in range of 350-4500 cm^{-1}.

3. Results and Discussion

3.1. P adsorption isotherm and Freundlich's n and k parameters

Phosphate adsorption isotherm was obtained by applying P solution at range concentration of 0 – 50 mM indicating that majority of P ion was adsorbed by amorphous mineral clay (>98%). Addition of humic acid nonsignificantly reduced adsorption of P on the amorphous mineral. This was likely related to the estimation method for calculating the amount of P adsorption. The calculating method for determining the amount of P adsorption was just done by subtracting the amount of P addition with P concentration remained in the equilibrium condition. This method resulted as rough data, because the amount of P adsorption was a total adsorption and we cannot differentiate the P complex forms such as innersphere complex, outersphere complex, partitioning and precipited one. Phosphate in outersphere complex form may be able to be taken up by plants. This is due to the plant roots secrete a mucigle that contain some organic acids such as acetic, oxalic, citric, malic, etc. The organic acids which are able to make a water-insoluble P, can be taken up by plants [14-18]. Although the concentration of the low molecular weight organic acids in soils is not as high as that of high molecular weight organic compounds, such as humic acid and fulvic acid, their role in soil environment is of great importance. Low molecular weight aliphatic and aromatic acids may block reactive adsorption sites on soil materials and thus reduce P adsorption [19-22]. Humic acid and silisic acid resulted a similar impact in P adsorption on allophane. Nevertheless there is some data that show the ability of silicate to block P better than humic acid. Adsorption experiment was done by addition of P

solution until 1000 ppm on Andisol that has not indicated saturation yet [23]. This reinforces the opinion that Andisol of central Java is a very strong soil in adsorb P (> 98%).

Reaction of HA or SA with allophane may have a side effect on partial dissolution of the allophane resulted in a breakdown of Si-O-Al bond, so a new reactive aluminol groups (≡Al-OH or ≡Al-OH_2) appeared. Aluminol has an important role in adsorbing phosphate [4]. By applying molecular orbital analyses method could be predicted that there are possibility phosphate anion adsorbed by silanol functional groups (≡Si-OH) even in a weak bonding [4].

In this case it might be some silanols from allophane-SA complexes role in adsorption of phosphate. Beside allophane, in the clay fraction also other amorphous materials such as imogolite and ferrihidrate were present and had a contribution in adsorbing P ion. All of active Al and Fe forms were normally determined with oxalate-oxalic acid pH 3. Higher content in allophane, also higher content in active Al (Alo) [24-25, 26], so the P adsorption capability of the soil also increased. High P adsorption percentage on allophane-humic or allophane-silicate complexes indicated that the both acids were not yet enough power for blocking P adsorption sites. In other words, that application of 100 mg l^{-1} of HA or SA were not enough for blocking 50 mM of P solution. In acid condition ≡Al-OH created positive charge of the soil due to entrancing H^+ ions on octahedral layer of $Al(OH)_3$ [27]. The phenomena could be written as follow:

$$Al(OH)_3 + H^+ \longrightarrow Al(OH)_3 ...H^+ \quad (1)$$

$$Al(OH)_3...H^+ + H_2PO_4^- \longrightarrow Al(OH)_3...H_3PO_4 \quad (2)$$

Based on the above equation it was indicated that in acid condition, phosphate ion adsorbed by allophane through electrostatic bond, so form a surface outersphere complex. The complex form is still likely to be exchanged by the other anions. While in pH 6 condition, the P adsorption phenomena might have occurred through a ligand exchange mechanism with reaction as follow:

$$Al(OH)_3 + H_2PO_4^- \longrightarrow Al(OH)_2H_2PO_4 + OH^- \quad (3)$$

Phosphate ion adsorbed by amorphous materials via ligand exchange mechanism formed innersphere complex [28]. Phosphorus adsorption by allophane collected from the four mountains located at Central Java was categorized as a high (> 98 %). Phosphate retention (PR) values for andisol from Tawangmangu and Kopeng (central Java) were 99 and 97 %, respectively [25].

Table 1. n and k parameters obtained from Freundlich equation for P sorption on allophane after HA addition at pH 4 and 6

Location	pH 4				pH 6			
	1/n	n	log k	k	1/n	n	log k	k
YS	0,38	2,6	1,335	21,63	0,37	2,7	1,388	24,43
OS	0,43	2,3	1,287	19,36	0,36	2,8	1,345	22,13
YD	0,26	3,9	1,510	32,36	0,38	2,6	1,275	18,84
OD	0,29	5,5	1,430	26,61	0,35	2,9	1,315	20,65
YM	0,31	3,2	1,399	25,06	0,31	3,2	0,389	24,49
OM	0,45	2,2	1,266	18,45	0,53	1,9	1,123	13,27
YL	0,29	3,5	1,590	38,91	0,22	4,6	1,727	53,33
OL	0,28	3,6	1,568	36,98	0,4	2,5	1,393	24,72

Table 2. n and k parameters obtained from Freundlich equation for P sorption on allophane after SA addition at pH 4 and 6

Location	pH 4				pH 6			
	1/n	n	log k	k	1/n	n	log k	k
YS	0,32	3,1	1,490	30,9	0,22	4,6	1,388	24,43
OS	0,33	3	1,425	26,61	0,2	5	1,734	54,20
YD	0,33	3	1,368	23,34	0,29	3,5	1,441	27,61
OD	0,3	3,3	1,415	26,00	0,34	2,9	1,346	22,18
YM	0,38	2,6	1,255	17,99	0,32	3,1	1,395	24,83
OM	0,3	3,3	1,412	25,.82	0,24	4,2	1,515	32,73
YL	0,3	3	1,426	26,67	0,32	3,1	1,383	24,16
OL	0,3	3,3	1,439	27,48	0,34	2,9	1,346	22,18

Freundlich isoterm equation was fit to descript P adsorption characteristic on allophane treated with HA and SA. Addition of HA and SA with rate of 100 mg L-1 was not so effective to reduce P adsorption. However, silicic acid tend stronger than humic acid in decreasing P adsorption in the pH 4 and 6 conditions. Based on the Freundlich equation, the affinity (n) and sorption capacity (k) of allophane-HA and allophane-SA could be calculated as presented at Table 1 and 2. Amorphous materials collected from the old mountain formation and treated with HA at

pH 4 and 6 were obtained higher sorption capacity (k) values than young one, but for the affinity values (n) were obtained varies. In case of treated with SA at pH 4 and 6 were obtained varies of k and n values.

3.2. Infrared Spectral Characteristics

Infrared spectral characteristics of eight allophane samples taken from 4 mountains in central Java and after treated with humic acid and silisic acid were presented in Figure 1, 2, 3, and 4. Infrared spectral characteristics of the amorphous mineral indicated four major adsorption band derived from stretching vibration of OH groups, deformation of H-O-H from adsorbed water, Si-O-Al bond, and Al-hydroxide (Al-OH struktural) ion polymers which they appeared at range of 3449 – 3510 cm^{-1}, 1639 – 1655 cm^{-1}, 972-1040 cm^{-1} and 530-570 cm^{-1}. Reaction of the anions with the amorphous material resulted in a shift of the four major adsorption band, each of them appeared at frequency of 3448,72; 1635,64; 1026,31 and 524,64-555,5 cm^{-1}. The shift of the first adsorption band was derived to OH from aluminol groups replaced by phosphate, carboxylate, silicate ions through ligand exchange. Strengthening on the peak adsorption band indicated that stretching vibration intensity of OH increased due to adsorption of the anions. A new adsorption band also appeared at frequency of 910,47 cm^{-1} on amorphous material sample taken from Dieng mountain. It was likely to be derived from stretching vibration of Al_2-OH.

Figure 1 (YS) shows the infrared spectral characteristics of allophane samples from the Mt. Young Slamet. Based on the picture, stretching vibration of hydroxyl groups (OH), HOH deformation of the adsorbed water, the bond Si-O-Al and Al-hydroxide, respectively appear at frequencies 3483, 1651, 972.1 and 570 cm-1. Whereas the samples from the Mt. Old Slamet appeared at 3448.5; 1647.1; 972.1 and 570.9 cm-1 (Fig 1-OS). Reaction with HA or SA resulted in a shift in the four main absorption band, each appearing at a frequency of 3448.72; 1635.64; 1026.31 and 524.64 to 555.5 cm^{-1}. Peak shift of the first absorption band was partly because aluminol OH group is replaced by a phosphate ion, carboxylate and silicate through a ligand exchange process. Reinforcement at the peak of the absorption band showed an increase in the intensity of stretching vibration of OH groups carried by the anion-anion exchanger. The same thing happens at the peak of the second absorption band. Here the peak of the absorption band was also shifted to lower frequencies. This was probably because part water adsorbed by amorphous mineral was replaced by the anions. While strengthening the intensity at the peak of the absorption band indicates the addition of water carried by the anion-anion exchanger. At the peak of the third absorption band, the frequency tends to shift toward the higher, from 972.1 to 1026.13 cm-1, likely this is due to the contribution of the vibrating group P = O stretching of phosphate ions that often arise in frequency of about 1026 cm and Si-O at a frequency of 1050 cm^{-1}. In contrast to the fourth peak of the absorption bands tend the frequency shift towards lower, i.e. from 570 to 555.5 cm^{-1} for the treatment at pH4 and to 524.6 cm^{-1} at pH 6. This is probably caused by the reaction of Al-hydroxide complex formation with the ligand anion exchanger (phosphate, carboxylate of humic and silicate).

Figure 1 (OS) shows the infrared spectral characteristics of the amorphous clay from Mt. Old Slamet has similarities with that of Mt. Young Slamet. The difference lies only in the peak of the third and fourth absorption band. Treatment with phosphate, humic-phosphate and silicate-phosphate and pH adjusted at 4 caused each frequency of the absorption band peak tends to shift from 972.1 to 925.27 cm^{-1} and 570.9 to 532.35 cm^{-1}. The same thing also happened at the treatment of pH 6, the frequency of the fourth absorption band peak shift towards the lower one (from 570.9 to 547.76 cm^{-1}). Clay fraction derived from Mt. Old Slamet was besides containing allophane-imogolit also contains bayerit or $Al\text{-}(OOH)_3$. At pH 4, Al-OH form either of allophane and bayerit tend to form $Al\text{-}OH_2^+$ so not much phosphate ions that form complexes with the amorphous mineral. While at pH 6 so many phosphate ions adsorbed by aluminol group through ligand exchange mechanism that is not easily desorbed. Therefore at pH 6, the frequency of the third absorption band peak shifted to a higher one (from 972.1 to 995.27 cm^{-1}.

Figure 2 shows the infrared spectral characteristics of allophane collected from the young and old formation of Mt.Dieng. Based on the picture, stretching vibration of hydroxyl groups (OH), HOH deformation of the adsorbed water, the bond Si-O-Al and Al-hydroxide, each appearing at a frequency of 3510.2 & 3483.2; 1654.8 & 1647,1; 1037.6 &1033, and 559.3 cm^{-1}, respectively. For sample from Old Dieng appears a new absorption band at a frequency of 910.47 cm^{-1}. The fequency is likely derived from Al_2-OH stretching vibration. The addition of phosphate anions, humic and silicate causes a shift in the four main absorption band, each appearing at a frequency of 3425.5 to 3441; 1635.64, and 1041.56 cm^{-1}. Peak shift of the first absorption band is due partly aluminol OH group is replaced by a phosphate ion, carboxylate and silicate through a ligand exchange process. Reinforcement at the peak of the absorption band showed an increase in the intensity of stretching vibration of OH groups carried by

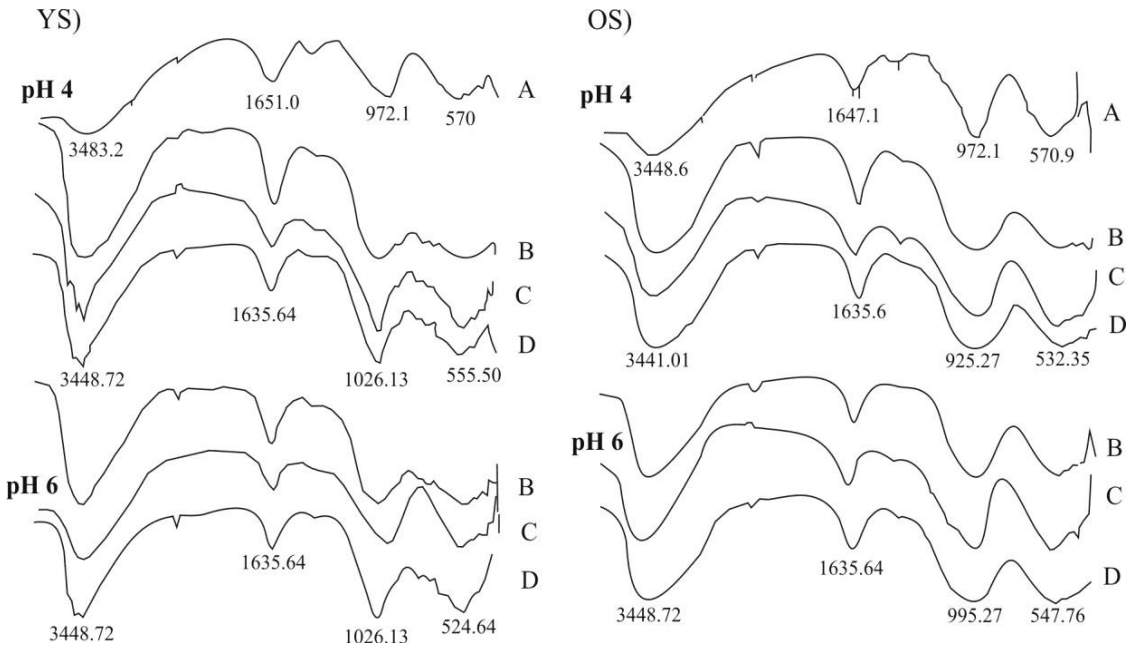

Fig. 1. Infrared spectral characteristics of allophane, allophane-P, Allophane-HA-P, Allophane-SA-P at pH 4 and 6 (samples from YS and OS)

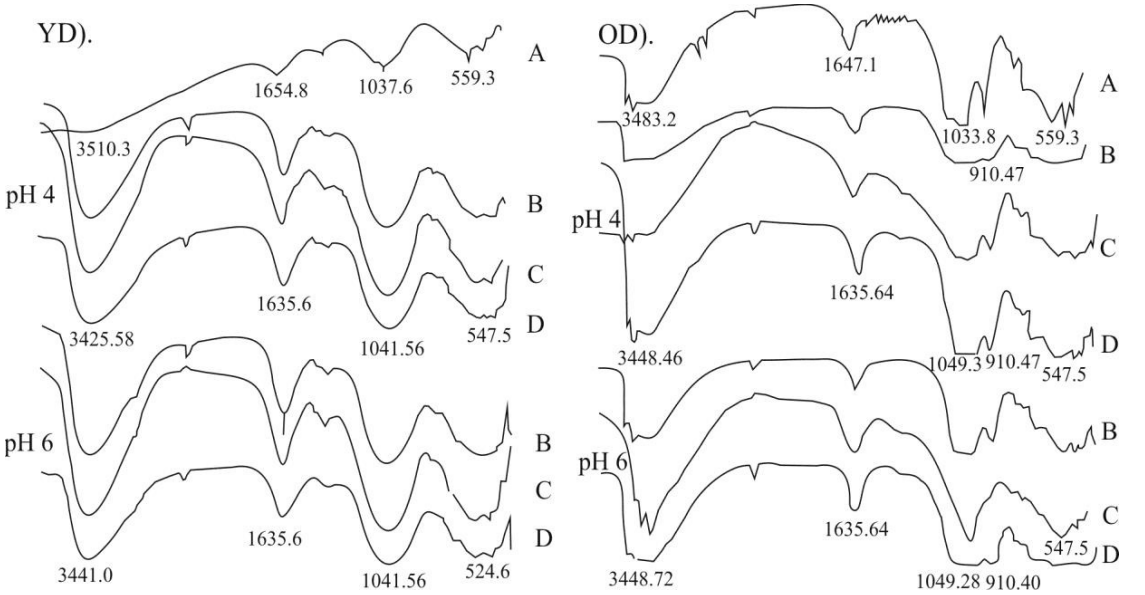

Fig 2. Infrared spectral characteristics of allophane, allophane-P, Allophane-HA-P, Allophane-SA-P at pH 4 and 6 (samples from YD and OD).

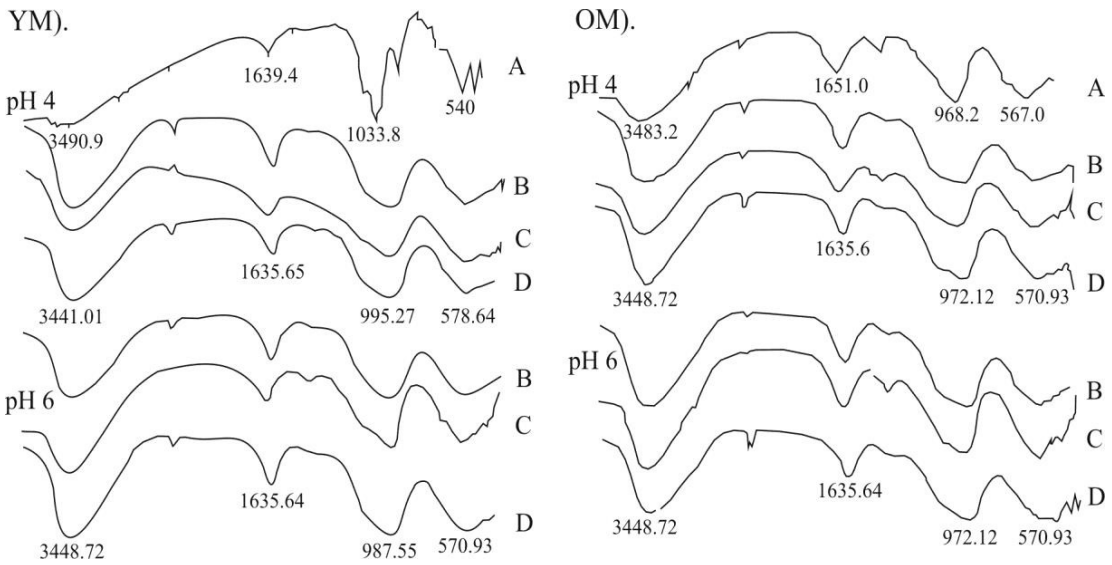

Fig 3. Infrared spectral characteristics of allophane, allophane-P, Allophane-HA-P, Allophane-SA-P at pH 4 and 6 (samples from YM and OM)

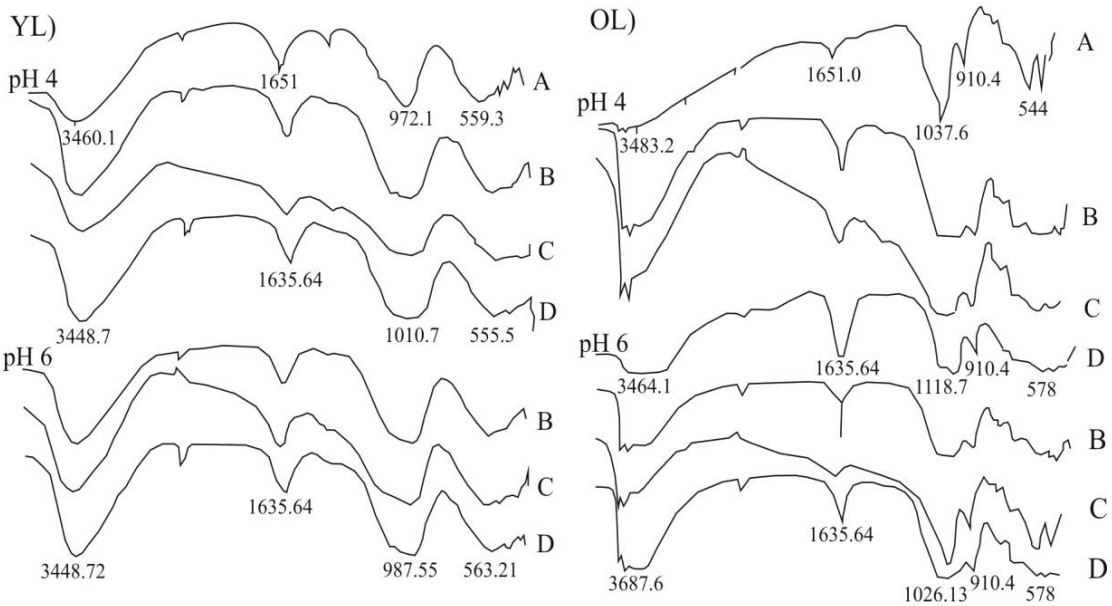

Fig 4. Infrared spectral characteristics of allophane, allophane-P, Allophane-HA-P, Allophane-SA-P at pH 4 and 6 (samples from YL and OL)

the anion-anion exchanger. The same thing happens at the peak of the second absorption band. Here the peak absorption band is also shifted to lower frequencies. This was probably due in part water adsorbed by amorphous mineral is replaced by the anions. While strengthening the intensity at the peak of the absorption band indicates the addition of water carried by the anion-anion exchanger. At the peak of the third absorption band, the frequency tends to shift toward the higher, from 1037.6 to 1041.5 cm^{-1}, likely this is due to the contribution of the vibrating group P = O stretching of phosphate ions that often arise in frequency of about 1026 cm Si-O and at a frequency of 1050 cm^{-1}. Effect of pH tended to shift the peak frequency of the fourth absorption band toward lower, i.e. from 559.3 to 547.5 cm^{-1} at pH4 and to 524.6 cm^{-1} at pH 6. This is probably caused by the reaction of Al-hydroxide complex formation with the ligand anion exchanger (phosphate, carboxylate of humic and silicate)

Allophane collected from the Mt. Old Dieng (Fig.2 OD) shows sorption of phosphate anions, humic-phosphate and silicate-phosphate at pH 4 and 6. Treatment at pH 4 and pH 6 caused a frequency shift of the fourth peak of absorption band in the same direction that the first absorption band shifts from 3483.2 to 3448.4 cm^{-1}, the second absorption band from 1647.1 to 1635.6 cm^{-1}, the third absorption band from 1033.8 to 1049.28 cm^{-1}, and the fourth absorption band from 559.3 to 547.5 cm^{-1}. While the peak position of an additional absorption band at a frequency of 910.47 does not shift at all. This indicated that Al_2-OH form was not reactive.

Figure 3 (YM, OM) shows the infrared spectral characteristics of allophane samples collected from young (YM) and old formation (OM) of Mt.Merbabu. Based on the picture, stretching vibration of hydroxyl groups (OH), HOH deformation of the adsorbed water, the bond Si-O-Al and Al-hydroxide, each appearing at a frequency of 3490.9 & 3483.2; 1639.4 & 1651; 1033.8 & 968.2 and 540 & 567 cm^{-1}. Allofan from YM (Fig.3) after complexation with phosphate anions, humic-phosphate and silicate-phosphate caused a frequency shift of the first absorption band peak of 3490.9 to 3441.01 cm^{-1} at pH 4 and to 3448.72 cm^{-1} at pH 6. The second peak absorption band shifted from 1639.4 to 1635.6 cm^{-1}, both at pH 4 and 6. The third peak absorption band shifted from 1033.8 to 995.27 cm^{-1} at pH 4 and to 987.55 cm^{-1} at pH 6. Being the fourth peak absorption band shifted from 540 to 578.6 cm^{-1} at pH 4 and to 570.93 cm^{-1} at pH 6. In case of Allophane from OM (Fig. 3), the frequency shift of the four peaks of the absorption band in the same direction that the first absorption band shifted from 3483.2 to 3448.4 cm^{-1}, the second one from 1651 to 1635.6 cm^{-1}, the third one from 968.2 to 972.12 cm^{-1} and the fourth one from 567 to 570.93 cm^{-1}. The intensity of the four absorption bands increased due to adsorption of HA-P and SA-P.

Figure 4 (YL & OL) shows the infrared spectral characteristics of allophane collected from Mt.Young Lawu (YL) and Old. Based on the picture, stretching vibration of hydroxyl groups (OH), HOH deformation of the adsorbed water, the bond Si-O-Al and Al-hydroxide, each appearing at a frequency of 3460.1 & 3483.2; 1651; 972.1 & 1037, 6 and 559.4 and 544 cm^{-1}. Sample from old lawu also appeared a new absorption band at a frequency of 910.47 is likely derived from Al_2-OH stretching vibration. After treatment with HA and SA, frequency due to stretching vibration of Al_2-OH did not shift at all. This indicated that Al_2-OH was not reactive form.

Allofan sample from Mt. Young Lawu (Figure 4-YL) shows the peak of the first absorption band and the second after treatment with phosphate, humic-phosphate and silicate-phosphate at pH 4 and 6 are likely to shift to the same frequency. Peak of the first and second absorption band each shifted from 3460.1 to 3448.7 cm^{-1} and from 1651 to 1635.6 cm^{-1}. The third absorption band peak shifted from 972.1 to 1010.7 cm^{-1} at pH 4 and to 987.55 cm^{-1} at pH 6. While the fourth absorption band peak shifted from 559.3 to 555.5 cm^{-1} at pH 4 and to 563.2 cm^{-1} at pH 6. In case of reaction allofan from Mt. Old Lawu (Figure 4-OL) with the anions resulted a frequency shift of the first absorption band peak from 3483.2 to 3464.1 cm^{-1} at pH 4 and to 3687.6 cm^{-1} at pH 6. The second peak absorption band shifted from 1651 to 1635.6 cm^{-1}, both at pH 4 and 6. The third peak absorption band shifted from 1037.6 to 1118.7 cm^{-1} at pH 4 and to 1026.13 cm^{-1} at pH 6. While the fourth peak absorption band shifted from 544 to 578 cm^{-1} both at pH 4 and 6.

4. Conclusion

Amorphous minerals collected from the four mountain in Central Java were categorized as very high in adsorbing phosphate anion (> 98 %) and fit with the Freundlich equation. Substracting the amount of P addition with P concentration remained in the equilibrium condition is a rough method, because the amount of P adsoprtion was a total adsorption, we cannot differentiate the P complex forms such as innersphere complex, outersphere complex, partitioning and presipited one. Infrared spectral characteristics of the amorphous material indicated that the main absorption bands appeared at a range of 3440-3510 cm^{-1} (due to stretching vibration of all hydroxyl (OH) groups, 1639-1655 cm^{-1} (adsorbed HOH), 910-972 cm^{-1} (Si-O-Al for allophane with low Si/Al ratio) or 1033 - 1030 cm^{-1}

(high Si/Al ratio). Complexation amorphous clay with humic acid or silicate acid caused the peak OH, Si-O-Al and Si-O adsorpstion move to the right and increase the adsorpstion intensity.

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